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“Effects of Colloids, Flocculation, Particle Size, and Organic Matter
on the Adsorption of Hexachlorobenzene to Sediments”

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of the requirements for the degree of

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in

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by

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ABSTRACT

“Effects of Colloids, Flocculation, Particle Size, and Organic Matter on the Adsorption of Hexachlorobenzene to Sediments”

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Understanding and quantifying the dynamics of the sorption and partitioning of contaminants to sediments is essential in understanding and predicting the transport and fate of hydrophobic contaminants. In the present study, the effects of colloids from the sediments and from the water, floc density and size, particle size, and organic matter on hexachlorobenzene (HCB) adsorption and partitioning have been quantified, which is achieved by the partition coefficient, K_p , defined as the ratio of contaminant associated with the sediment to the contaminant associated with the filtrate. It is shown that the measured steady-state partition coefficient increases due to the colloids initially present in the water that aggregate to the sediment compartment. Also, colloids initially associated with the sediment decrease the measured steady-state partition coefficient by dissociating from the sediment and dissolving in the water where they are measured in the dissolved compartment. Experiments also conclude the majority of adsorption is due to the organic matter present in the sediment. It will be shown that adsorption rates are almost an order of magnitude faster for smaller particles than for larger particles, and that adsorption rates are an order of magnitude slower for higher density flocs caused by high concentrations of sediment, than for lower density flocs. Finally, it will be demonstrated that adsorption to particles is an order of magnitude faster than adsorption to flocs consisting of the same particles.

TABLE OF CONTENTS

Introduction	1
Experimental Procedures and Sediment Properties	3
Results and Discussion of Sorption Experiments	10
Summary and Concluding Remarks	18
References	21
Tables	24
Figures	28
Appendix	38

INTRODUCTION

The sorption and partitioning of organic chemicals to sediments and soils are essential factors in determining the phase distributions, bioavailability, and long-term fate of these chemicals in aquatic environments. Considerable experimental, field, and theoretical work concerned with the sorption and partitioning of organic chemicals to sediments and soils has been done. For example, see reviews by Di Toro et al [1], Sawhney and Brown [2], and Baker [3]. In much of this work, it has been assumed that sorption occurred rapidly and therefore that chemical equilibrium existed. However, recent work [4, 5, 6] has indicated that sorption processes can be quite slow and therefore that chemical equilibrium may not be a good approximation in many cases.

In particular, recent experimental work [7] on the adsorption and partitioning of hexachlorobenzene (HCB) to natural sediments has shown quite clearly that these processes can be relatively slow, with up to 50 days required before a steady-state equilibrium was attained. These experiments were batch mixing experiments and were conducted for long times (up to six months) in order to be certain that a steady-state had been reached. The experiments were also done at different sediment concentrations from 10 to 10,000 mg/L. In all cases, a steady-state equilibrium was attained.

In these experiments, the mixtures that were tested consisted of HCB, natural sediments from the Detroit River, and tap water. The water was filtered with a 0.2 μm filter before use. Nevertheless, the effects of the colloidal matter inherently in this water, even after filtration, were significant. However, by correcting for this factor, it was demonstrated that in the steady state a true

chemical equilibrium existed and this equilibrium was independent of the solids concentration, the initial conditions of the experiment, and the path to equilibrium.

The effects of the colloidal matter from the tap water were the dominant factor in the measured partitioning at low sediment concentrations, although some effects were evident at all sediment concentrations. These effects will be different for different waters (e.g., unfiltered and filtered tap water, river and lake waters, and oceanic waters) but will generally be a significant factor in measuring and determining sorption and partitioning for all waters. The flocculation and sorptive properties of the colloids in these waters are not well understood and need to be investigated further.

However, in the experimental work reported here, it was decided to eliminate the effects of these colloids by using pure water in the experiments as much as possible. The results of these experiments can then be compared with the previous results by Jepsen et al [7] to more quantitatively determine the effects of the colloids in the tap water. In addition, further experiments have been done in order to more accurately quantify the adsorption rates, the partitioning, and especially the factors affecting these quantities. In particular, we have quantitatively investigated the effects of colloids inherently in the water, colloids associated with the sediments, floc density and size, particle size, and the organic content of the sediments. Some of these factors have been investigated previously by other investigators, but only in short-term experiments. The present experiments are all long-term equilibration experiments. All experiments were done with HCB and with the same sediments from the Detroit River as in the experiments by Jepsen et al. Some were done with the original composite sediments, while others were done with different size fractions of these sediments.

In the following section, the experimental procedures for the adsorption

experiments are briefly described. Pertinent properties of the composite and size-fractionated sediments are also described. All fine-grained sediments flocculate to some extent, and it will be shown below that this flocculation has a significant effect on the sorption process. Because of this, flocculation experiments were done in order to quantitatively describe the flocculation process and the properties of the flocs for the sediments used here. The experiments and pertinent properties of the flocs are also reported in the following section. The results and a discussion of all adsorption experiments are then presented in the third section. A summary and concluding remarks are given in the final section.

EXPERIMENTAL PROCEDURES AND SEDIMENT PROPERTIES

Basic Adsorption Experiments

The basic adsorption experiments were done in the same manner as described by Jepsen et al [7]. Because of this, only a brief description of the experimental procedures is given here. The experiments were done with carbon-14 labeled HCB in order to simplify the experiments and enhance sensitivity. In the experiments, HCB and sediments at concentrations from 2 mg/L to 10,000 mg/L were mixed with Optima pure water, the mixtures placed in amber Qorpak glass jars with teflon lined lids, and the jars were then rotated for various periods of time until they were sampled. Experiments were conducted for different periods of time up to six months.

Carbon-14 labeled HCB with a specific activity of 10.8 mCi/mmole was obtained from Sigma Chemical. The HCB was transferred with 25 mL of iso-octane to a 50 mL amber Qorpak jar. Aqueous stock solutions were made by plating 2.5 mL of the HCB in iso-octane onto the inner walls of a 1 L amber

bottle. After the solvent evaporated, the bottle was filled with pure water, and the HCB then dissolved in the water. This stock solution was stirred for at least one week before use. Just before use, the solution was filtered with a 1 μm pore size filter in order to separate out any undissolved HCB. Sufficient radioactivity was added to each experiment to ensure detectable levels in all measured compartments. All samples were counted on an LKB Wallace 1217 Rackbeta Liquid Scintillation Counter with corrections for quenching.

Desired sediment concentrations were prepared by diluting the original sediment with pure water. Sediment concentrations were determined by filtering 50 mL of the mixture through tared 0.45 μm Millipore filters, drying the filter, and determining the weight of the sediment residue.

The samples were prepared by placing the HCB stock solution and an amount of a sediment-water mixture sufficient to achieve the desired sediment concentration into a 125 mL Qorpack jar filled with pure water. The jar was immediately shaken. The total HCB added to each experiment was approximately 3×10^{-4} mg; the resulting HCB concentration was approximately 2.4 $\mu\text{g/L}$, and this same concentration was used in all experiments. The bottle was then placed on a rolling table and rotated at approximately 6 rpm. One sample jar was prepared for each sample point.

The amounts of HCB sorbed to the solid and dissolved in the water were then determined by filtration and measurement of the radioactivity on the filter and in the filtrate. Since the amount of radioactivity sorbed by the filter has been shown to be negligible, the amount of radioactivity on the filter was due almost entirely to the filtered sediment. The mass of the filtered sediment was weighed as described above.

For a mixture of sediment with mass, m_{sed} , and water with volume, V , the partition coefficient, K_p , is defined as

$$K_p = \frac{C_s}{C_w} \quad (1)$$

where $C_s = m_{\text{Hs}}/m_{\text{sed}}$ and is the mass of HCB sorbed to the sediment, m_{Hs} , divided by the mass of the sediment, and $C_w = m_{\text{Hd}}/V$ and is the mass of HCB dissolved in water, m_{Hd} , divided by the volume of water. The partition coefficient was calculated from this equation using the data obtained as described above.

Experiments were done with considerable attention to optimizing precision. More than one-third of all data points were replicated. The overall precision for $\log K_p$ is estimated to be ± 0.1 .

Particle Size Distributions

In order to obtain the disaggregated size distribution of the sediments, the sediments were first stirred vigorously using a blender. The particle size distribution was then measured using a Malvern particle sizer. This distribution is shown in Figure 1a. It can be seen that the median size of the disaggregated particles is about 7 μm with approximately 90% of the particles below about 30 μm .

In order to investigate the sorption characteristics of different size fractions of the sediments, the sediments were separated into four different size fractions. This was done as follows. The sediments were first passed through a 63 μm screen and then through a 38 μm screen. The sediments retained on the 38 μm screen were taken as one size fraction; the median diameter of these sediments was 53 μm . The sediments that passed through the 38 μm screen were then separated

by differential settling into three further size fractions with median diameters of 3, 7, and 17 μm . The size distributions of these four size fractions are shown in Figure 1b. It should be noted that, because of the separation process and loss of both very large and very small particles, the original sediment is not a weighted average of the four size fractions shown in Fig. 1b.

It will be shown below that the different size fractions have different organic contents and mineralogies. In order to do adsorption experiments where the only difference between the sediments was the particle size, some of the 53 μm sediments were crushed so as to reduce them in size. The resulting size distribution is shown in Figure 1b. The median size of the crushed 53 μm sediments is about 14 μm .

Organic Carbon Content

The total carbon contents of the composite and size-fractionated sediments were determined by the Analytical Laboratory at UCSB using a Control Equipment Corporation Model 240 XA Elemental Analyzer and are shown in Table 1. In order to determine the organic carbon content of the sediments, the following procedure was used [8]. Hydrochloric acid (HCl) was added to the sediments at a ratio of 5 mL of HCl to 1 g of sediment; the mixture was kept at 80°C overnight. The acid reacted with the inorganic carbon (carbonates) to produce carbon dioxide which then left the sediments as a gas. Total carbon of the remaining sediment residue was then determined and is reported here as organic carbon (see Table 1). For the composite sediment, the organic carbon content was determined to be 1.42%; for the size fractions of 3, 7, 17, and 53 μm , the organic carbon content was 1.62, 1.45, 1.02, and 3.32% respectively. In the 53 μm fraction, large

chunks of organic matter were visible through a microscope; these chunks were not visible in the smaller size fractions. These large chunks in the 53 μm fraction probably account for the larger percentage of organic matter in the size fraction as compared to the smaller size fractions. Their presence may also indicate that the organic carbon in the 53 μm size fraction may be of a different type or quality than in the other size fractions.

In order to determine the effects of organic matter on sorption, some experiments were duplicated except that the organic matter was removed from the sediments. This was done by treating the sediments with a sodium hypochlorite (NaOCl) solution [9]. This solution was obtained from the Fisher Scientific Company and contained 4 to 6% available chlorite. The solution was then adjusted to a pH of 9.5. Approximately 1 g of sediments was suspended in 20 mL of NaOCl in a 50 mL centrifuge tube. The mixture was then set in a boiling water bath for 30 minutes while shaken to ensure that the sediments were kept in suspension. After this, the mixture was put in a centrifuge for 10 minutes at 800 rpm to separate the sediments from the supernatant. The solution was then decanted. This treatment was repeated at least three more times to ensure almost complete elimination of the organic matter.

As a check on the procedures, the sum of the percent organic carbon remaining after HCl stripping and the percent inorganic carbon remaining after NaOCl stripping should equal the percent of total carbon initially in the sample. Table 1 shows the percentages and also shows that almost all carbon is accounted for.

Mineralogy

The mineralogy of the sediments was examined for each size fraction by use

of x-ray diffraction performed at the Department of Geological Sciences at UCSB. Identification of mineral constituents was determined by comparison to American Society of Testing Materials Mineralogy Standards. By this means, it was shown that the larger sizes of sediments (53, 17, and 7 μm) contained primarily quartz, calcite, dolomite, and feldspar. The 3 μm sediments contained these minerals, but also a higher amount of clay, specifically illite and chlorite. The relative abundance of clay is difficult to determine by x-ray diffraction; however, by use of a scanning electron microscope, it was determined that the 3 μm sediments contained a large amount of clay.

Flocculation Experiments

All fine-grained sediments flocculate to some extent. As will be shown later, this flocculation has a significant effect on the sorption process. From previous experimental and theoretical work on flocculation [10, 11, 12], the flocculation process is reasonably well understood. However, in order to illustrate the flocculation process and quantitatively determine the significant flocculation parameters for the sediments used here, flocculation experiments with the present sediments were done.

In order to simulate the flocculation process in the sorption experiments, mixtures of disaggregated sediments and water at sediment concentrations from 2 to 10,000 mg/L were placed in 125 mL Qorpak bottles, and the bottles rotated at 6 rpm. Measurements of floc size distributions were taken at intervals by sampling and using the Malvern particle sizer. For large flocs, the sizes were determined by direct observation and measurement.

Typical results for the median diameter of the flocs as a function of time are shown in Figure 2 for sediment concentrations of 100, 500, and 2000 mg/L. As

in previous experiments, the median floc size remains relatively small at first, increases rapidly over a short time interval, and then approaches a steady state. The steady-state median floc sizes and the approximate times to equilibrium for all sediment concentrations tested are shown in Table 2a. It can be seen that as the sediment concentration increases, the median floc size and the time to steady state decrease.

Settling Speeds and Densities of Flocs

Settling speeds of the steady-state flocs were also measured. This was done by directly measuring the settling speeds of the flocs in a settling tube in approximately the same manner as described by Burban et al [13]. For each sediment concentration, approximately 60 to 80 measurements of the settling speeds of flocs were taken and were then averaged. These average speeds are shown in Figure 3 as a function of the median diameter of the flocs at each sediment concentration. For comparison, the settling speeds as determined from Stokes Law for a solid particle with a density of 2.6 g/cm^3 are also shown. It can be seen that the settling speeds increase as the floc diameter increases, but at a rate much slower than that predicted by Stokes law. The measured settling speeds are also listed in Table 1.

Stokes law for the settling speed, w_s , of slowly moving particles is given by

$$w_s = (\rho_p - \rho_w) \frac{gd^2}{18\mu} \quad (2)$$

where ρ_p is the density of the particle, ρ_w is the density of water, g is the acceleration due to gravity, d is the diameter of the particle, and μ is the molecular

viscosity of water. This equation is valid for Reynolds numbers ($Re = \rho_w w_s d / \mu$) less than 0.5. From this equation, an effective density for a floc, ρ_f , can be defined and is

$$\rho_f = \rho_w + \frac{18\mu w_s}{g d^2} \quad (3)$$

The effective densities for the steady-state flocs were then determined by use of this equation and the measured data on floc diameters and settling speeds; the resulting densities are listed in Table 1. It can be seen that, as the sediment concentration increases, the floc size and settling speed decrease but the floc density increases from a very low value close to that of water to a value close to that of a solid sedimentary particle (approximately 2.6 g/cm^3).

RESULTS AND DISCUSSION OF SORPTION EXPERIMENTS

Effects of Colloids

The present experiments are an extension of those reported by Jepsen et al [7]. These latter experiments were done with mixtures of sediments, HCB, and tap water. Despite the fact that the tap water had been filtered with a $0.2 \mu\text{m}$ filter before use, the effects of the colloidal matter remaining in the water on the partitioning of the HCB were evident at all sediment concentrations but were dominant at low concentrations. The effects on the partitioning were due to the sorption of HCB to the colloids, the flocculation of these colloids, the subsequent filtering and retention of this flocculated colloidal matter on the filter, and the inclusion of the HCB sorbed to the flocculated colloidal matter as part of the HCB

sorbed to the solids. The measured partition coefficients are shown in Figure 4. It can be seen that $\log K_p$ varies from 4.37 for a sediment concentration of 10 mg/L to 3.67 for a sediment concentration of 10,000 mg/L.

In general, it was shown that the measured partition coefficient K_{pm} could be written in terms of the true partition coefficient K_p as

$$K_{pm} = K_p + \frac{m_{Hc}}{m_{Hd} C} \quad (4)$$

where m_{Hc} is the mass of HCB adsorbed to the flocculated colloidal matter, m_{Hd} is the mass of HCB dissolved in the water, and C is the sediment concentration. The ratio of m_{Hc} to m_{Hd} can be determined independently from mixing experiments with just HCB and water. Once this ratio is known, K_p can be calculated. It has been shown that the above equation is in excellent agreement with the experimental results.

In the experiments by Jepsen et al, it was difficult to accurately determine the rates of HCB adsorption because of the confounding effects of the colloidal matter from the water. In order to eliminate these effects, subsequent sorption experiments were done in pure water and are reported here. The experiments were done at sediment concentrations of 2, 10, 100, 500, 2000, and 10,000 mg/L. The results for $\log K_p$ as a function of time are shown in Figure 5.

It can be seen that the steady-state equilibrium partition coefficient still depends on the sediment concentration, although the dependence is relatively small ($\log K_p = 4.0$ for a sediment concentration of 2 mg/L and decreases to 3.78 at a sediment concentration of 10,000 mg/L). In addition, it can be seen that sorption is relatively fast at low concentrations (less than one day to equilibrium at 2 mg/L) but increases as the sediment concentration increases (approximately 30 to 40 days

to equilibrium at 10,000 mg/L).

In the present experiments, no colloidal matter is present in the pure water. However, there is colloidal matter in the sediment solution introduced into the HCB-pure water mixture. This matter is inherent in any natural sediment-water mixture. In general, HCB will be truly dissolved in the water and also adsorbed to the solid sedimentary particles, to the colloidal matter, and to the flocculated colloidal matter. In the present experiments, the mass of HCB adsorbed to the flocculated colloidal matter is generally small by comparison with the HCB adsorbed to the solid particles and will therefore be ignored.

Denote the mass of HCB on the colloidal matter by m_{Hdc} . The amount of HCB retained on the filter consists of the HCB sorbed to the sediments, while the amount of HCB in the filtrate consists of the truly dissolved HCB plus the amount of HCB sorbed to the colloidal matter from the sediments. It follows that the measured partition coefficient in this case is given by

$$\begin{aligned}
 K_{pm} &= \frac{\frac{m_{Hs}}{m_{Hd} + m_{Hdc}}}{\frac{m_{sed}}{V}} = \frac{\frac{m_{Hs}}{m_{sed}}}{\left(\frac{m_{Hd}}{V}\right) \left(1 + \frac{m_{Hdc}}{m_{Hd}}\right)} \\
 &= \frac{K_p}{1 + \frac{m_{Hdc}}{m_{Hd}}}
 \end{aligned} \tag{5}$$

In general, the mass of the colloidal matter from the sediments, m_{dc} , should be proportional to the mass of the sediments, i.e., $m_{dc} = N m_{sed}$, where N is the fraction of colloidal matter. A partition coefficient for the colloidal matter can be defined as

$$K_c = \frac{\frac{m_{Hdc}}{m_{Hd}}}{\frac{m_{dc}}{m_{Hd}}} \quad (6)$$

It follows that

$$\begin{aligned} \frac{m_{Hdc}}{m_{Hd}} &= K_c \frac{m_{dc}}{m_{Hd}} = K_c N \frac{m_{sed}}{V} \\ &= K_c NC \end{aligned} \quad (7)$$

By substituting this expression into Eq. (5), one obtains

$$K_{pm} = \frac{K_p}{1 + K_c NC} \quad (8)$$

It can be seen that K_{pm} reduces to K_p as the sediment concentration C decreases to zero. From this and Figure 4, it follows that the log of the true equilibrium partition coefficient K_p is approximately equal to 4.0 ± 0.1 , or $K_p = 10,000$.

If it is further assumed that the partition coefficient for the colloidal matter is approximately the same as that for the sediments, it follows that

$$K_{pm} = \frac{K_p}{1 + K_p NC} \quad (9)$$

This is the same expression as that derived by Gschwend and Wu [14]. From this equation and the data in Figure 5, N can be determined and is approximately 0.005, a reasonable number for the fraction of colloidal particles (less than 1 μm)

in natural sediments. It can be seen that, at least for the present sediments, the effects of the colloids from the sediments are relatively small by comparison with the effects of the colloids in tap water.

The combined effects of the colloids from the water and from the sediments can be described by

$$K_{pm} = \frac{K_p}{1 + K_c NC} + \frac{m_{Hc}}{m_{Hd}C(1 + K_c NC)} \quad (10)$$

Effects of Flocculation and Particle Size

Figure 5 shows that the time to steady state is relatively short at 2 mg/L (less than one day) but increases as the sediment concentration increases so that it is about 30 days at a sediment concentration of 10,000 mg/L. This can be attributed to the flocculation of the particles. At first, this attribution may seem incorrect since the median floc size at 2 mg/L (4500 μm) is much greater than the median floc size at 10,000 mg/L (17 μm). If it is assumed that the time to steady state is governed by the HCB diffusion into a floc and that this time increases as the floc size increases, then the time to the steady state should be much greater for the larger flocs at 2 mg/L than for the smaller flocs at 10,000 mg/L.

However, at 2 mg/L, although the floc sizes are quite large, the floc densities are quite small ($\rho_f = 1.0009 \text{ g/cm}^3$, see Table 2), and the flocs are quite open and fragile (see [12] for photographs of these flocs). In addition, the flocculation time is relatively long (228 hours) so that almost all adsorption occurs before there is significant flocculation. The rate limiting step for HCB transfer is then the diffusion of HCB into the interior of the particle, and not transport through the floc.

In contrast, at 10,000 mg/L, the flocs are small, but quite dense (2.2 g/cm^3), quite stable, and they resist disaggregation [12]. In this case, flocculation is quite rapid (1.2 hours) and most adsorption therefore occurs after flocculation is complete. The transfer of HCB is now from the water to the floc, diffusion through the floc, and then diffusion into the interior of a particle in the floc. This combined process of diffusion into the floc and then into the particle is relatively slow and accounts for the long time to steady state for the sediments at 10,000 mg/L as compared to the sediments at 2 mg/L.

To further substantiate these ideas and also investigate the effects of particle size, four additional experiments were conducted. These experiments were done at 10 mg/L (where flocculation was slow and almost all adsorption occurred before there was significant flocculation) and at 500 mg/L (where flocculation was rapid and most adsorption occurred after flocculation was complete). For each concentration, experiments were done with 53 μm particles and with these same sediments crushed to a median size of 14 μm (referred to hereafter as crushed 53 μm particles); these two sediment samples obviously have the same mineralogy and organic content and differ only in their sizes. For these four cases, results for $\log K_p$ as a function of time are shown in Figure 6.

By comparison of the results for the 53 μm particles at 500 mg/L and at 10 mg/L, it can be seen that the time to equilibrium is much less at 10 mg/L (approximately 5 days) than it is at 500 mg/L (approximately 30 days). As above, this can be explained as due to the effects of flocculation of the particles. At 10 mg/L, flocculation is slow and takes almost 3 days to occur. Before 2 days, relatively little flocculation occurs and hence most sorption takes place as HCB is sorbed to individual particles. The sorption is therefore relatively fast. At 500 mg/L, flocculation occurs in less than 4 hours. In this case, most sorption occurs

original organic matter and is certainly possible since the organic removal procedure does not guarantee removal of all the organic matter in the sediments. Note that the time to steady state has also been reduced by the stripping of the organics, especially for the 53 μm sediments.

Adsorption to Different Size Fractions

Sorption experiments were also done with different size fractions of the sediments. As described before, these size fractions had median diameters of 3, 7, 17, and 53 μm . Log K_p as a function of time for these sediments at 500 mg/L are shown in Figure 8. It can be seen that qualitatively all curves are similar with the smaller particles reaching equilibrium faster than the larger particles. Additional data points were obtained at 120 days, are not shown here, but do demonstrate that all of the partitionings had reached a steady state at times less than 60 days. The gradual increase in K_p for long time that might be inferred from Figure 8 is just due to small uncertainties in the experimental data. The equilibrium partition coefficients of all size fractions are different with no obvious trend to the results. Since each size fraction has a different organic content, the results for K_p were normalized to the organic fraction, f_{oc} . The results for K_{oc} , which equals K_p/f_{oc} , are shown in Figure 9. The equilibrium partition coefficients are all still different. However, the values for K_{oc} now increase in a monotonic manner as particle size decreases. The steady-state K_p , K_{oc} , and K_p for the same sediments stripped of organic carbon are shown in Table 3.

The fact that K_{oc} increases as particle size decreases and hence as surface area increases (for the same mass) indicates that this effect may be due to surface sorption, which would increase as surface area increases. However, our previous experiments on 53 μm and crushed 53 μm particles do not indicate an effect of

after the particles have flocculated. HCB must then diffuse into the floc and then into the particles in the floc, a much slower process than simply diffusion into a particle.

By comparison of $\log K_p$ for the 53 μm particles and for the crushed 53 μm particles at 500 mg/L, it can be seen that the crushed particles reach equilibrium in 1 to 2 days while the uncrushed 53 μm particles reach the same equilibrium in approximately 30 days, i.e., the time to equilibrium depends on particle size and increases as the particle size increases. By comparison of the results for the 53 μm and crushed 53 μm particles at 10 mg/L, the same conclusion can be reached. Other experimental results not shown here also substantiate this result.

For the crushed 53 mm particles at 10 and 500 mg/L, the times to equilibrium are relatively short because of the small sizes of the particles and are approximately 1 to 2 days. No differences between the two cases are evident.

Effects of Organic Content

In order to determine the effects of the organic content of the sediments on the adsorption, experiments were done with the organic matter stripped from the sediments. For these experiments, results for $\log K_p$ as a function of time for the 53 μm and the crushed 53 μm particles at 500 mg/L are shown in Figure 7. It can be seen that the crushed particles reach equilibrium faster than the uncrushed particles as expected. By comparing Figure 7 with Figure 6, it can be seen that the equilibrium K_p 's for the particles stripped of organic matter are much lower than the K_p 's for the unstripped particles, by about a factor of 16. After stripping, the remaining sorption could be due to sorption of HCB to the mineral surfaces of the sediments or due to sorption of HCB to a small amount of organic matter still remaining in the sediments. This would have to be on the order of 5% of the

surface area on equilibrium partition coefficients. Other possibilities for the differences would be (a) the different quality of organic matter between the smaller and larger particles and (b) perhaps a greater dependence on surface area for very small particles, less than the 53 μm and crushed 53 μm particles. However, this effect (or effects) is relatively small and our present experiments are not sufficient to ascertain the cause.

Linearity of the HCB Isotherm

In the previous work by Jepsen et al, a linear isotherm was assumed in the analysis of the experiments. Therefore the partition coefficient is independent of the concentration of HCB dissolved in water. The excellent agreement between the experimental and theoretical results served to substantiate that assumption. As a direct verification of the linearity of the HCB isotherm, we have conducted experiments with pure water, sediments at a concentration of 10 mg/L, and HCB at concentrations from .02 to 5 $\mu\text{g/L}$, a change of more than two orders of magnitude. In all cases, $\log K_p$ was constant to within ± 0.1 , and therefore the HCB isotherm is linear over this range of HCB concentrations.

SUMMARY AND CONCLUDING REMARKS

Previous work by Jepsen et al has shown that sorption and partitioning of HCB to natural sediments can be relatively slow processes, but that eventually a steady-state equilibrium is attained from which a unique equilibrium partition coefficient can be determined. In their experiments, effects of HCB dissolution, the flocculation of the colloidal matter from the water, and the flocculation of the

sedimentary particles were shown to be significant.

The present experiments were done in pure water to eliminate the effects of the colloidal matter from the water. Nevertheless, colloidal matter is inherently present in any mixture of natural sediments and water. In the present experiments, the effects of the colloids from the sediments were evident; their effect on the measured partition coefficient can be described by Eq. (9). More generally, the effects on the measured partition coefficient of colloids from the sediments and from the water can be described by Eq. (10). From these experiments, the log of the equilibrium partition coefficient for HCB, the present sediments, and pure water was determined to be 4.0 ± 0.1 , or $K_p = 10,000$.

The rate of adsorption (and therefore the time to steady state) was significantly affected by the flocculation of the particles. At low sediment concentrations, the flocs were large but open and fragile, the rate of flocculation was low, HCB was transferred readily from the water to a particle in the floc, and the time to steady state was therefore determined by the time for diffusion of HCB into the particle. At high sediment concentrations, the flocs were small but dense, flocculation occurred rapidly, HCB was transferred from the water to the floc, diffused slowly into the floc, and then diffused into the particle. This is a relatively slow process compared to that occurring at low sediment concentrations.

Additional experiments also demonstrated directly that adsorption to particles was much faster than adsorption to flocs consisting of the same particles. Investigations of the effects of particle size demonstrated that smaller particles reached a steady state faster than larger particles.

A reduction in K_p by about a factor of 16 resulted from stripping the particles of organic content. It could not be ascertained whether the remaining partitioning was due to a residue of organic matter or due to adsorption to mineral surfaces.

The stripping also reduced the time to steady state, at least for the 53 μm sediments.

Investigations were made of size-fractionated sediments with median sizes of 3, 7, 17, and 53 μm . The size fractions differed in organic content and mineralogy. After normalizing the partition coefficients to organic fraction, the partition coefficients were still not all equal but decreased monotonically as the particle size increased.

In general, it has been shown that the measured steady-state partition coefficients depend on the amount of colloids from the water and from the sediments and on the amount of organic matter in the sediments. The adsorption rates depend on these quantities as well as the floc density and size and the particle size.

Similar experiments are presently being done with several different PCBs. The results are qualitatively similar to those described here and by Jepsen et al. Because of this, it is believed that the general conclusions presented here are probably valid for the adsorption and partitioning of most hydrophobic organic chemicals to sediments and soils.

REFERENCES

1. Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Barry, R.C. Schwartz, C.E. Cowan, S.P. Pavlov, H.E. Allen, N.A. Thomas, and P.R. Paquin, 1991, Technical Basis for Establishing Sediment Quality Criteria for Nonionic Organic Chemicals by Using Equilibrium Partitioning, *Environ. Toxicol. and Chem.*, **10**, 1541-1583.
2. Sawhney, B.L and K. Brown, 1989, Reactions and Movement of Organic Chemicals in Soils, Soil Science Society of America, *SSSA Special Publication*, No. 22, Madison, Wisconsin.
3. Baker, R.A., 1991, *Organic Substances and Sediments in Water*, Vols. 1, 2, 3, Lewis Publishers, Chelsea, Michigan.
4. Karickhoff, S.N. and K.R. Morris, 1985, Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspension, *Environmental Toxicology and Chemistry*, **4**, pp. 469-479.
5. Coates, J.T. and A.W. Elzerman, 1986, Desorption Kinetics for Selected PCB Congeners from River Sediments, *J. of Contam. Hydrol.*, **1**, pp. 191-210.
6. Van Hoof, P.L. and A.W. Andren, 1991, Partitioning and Sorption Kinetics of a PCB in Aqueous Suspensions of Model Particles: A Solids

Concentration Effect, in R.A. Baker, ed., *Organic Substances and Sediments in Water*, Vol. 2, Lewis Publishers, Chelsea, Michigan, pp. 149-167.

7. **Jepsen, R., S. Borglin, and W. Lick**, 1995, Parameters Affecting the Adsorption of Hexachlorobenzene to Natural Sediments, *Environmental Toxicology and Chemistry*, in press.
8. **Naidu, A.S.**, 1987, Distribution of Organic Carbon, Nitrogen and C_{org}/N Ratios of Glaciomarine Sediments of Port Valdez, Valdez Arm and Prince William Sound, South Alaska, SCOPE/UNEP Sonderbd. **64**, pp. 279-287.
9. **Anderson J.U.**, 1961, An Improved Pretreatment for Mineralogical Analysis of Samples Containing Organic Matter, *Tenth National Conference on Clay Minerals*, 380-388.
10. **Tsai, C.H., S. Iacobellis, and W. Lick**, 1987, The Flocculation of Fine-Grained Lake Sediments Due to a Uniform Shear Stress, *J. Great Lakes Research*, Vol. **13**, pp. 135-146.
11. **Lick, W. and J. Lick**, 1988, On the Aggregation and Disaggregation of Fine-Grained Sediments, *J. Great Lakes Research*, Vol. **14**, pp. 514-523.
12. **Lick, W., H. Huang, and R. Jepsen**, 1993, Flocculation of Fine-Grained Sediments Due to Differential Settling, *J. Geophys. Res.*, **98**, C6,

pp. 10279-10288.

13. **Burban, P.Y., Y.J. Xu, J. McNeil, and W. Lick**, 1990, Settling Speeds of Floccs in Fresh Water and Seawater, *J. Geophysical Research*, **95**, pp. 18213-18220.

14. **Gschwend, P.M. and S.C. Wu**, 1985, On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants, *Environ. Sci. Technol.*, **19**, pp. 90-96.

TABLE 1

Percentage of Total Carbon, Organic Carbon, and Inorganic Carbon
for Composite and Size-fractionated Sediments.

Sediments	% Total Carbon (untreated)	% Organic Carbon (HCl stripped)	% Inorganic Carbon (NaOCl stripped)	% Carbon Unaccounted For
Composite	4.04	1.42	2.42	0.20
3 micron	2.75	1.62	1.07	0.06
7 micron	3.60	1.45	1.99	0.16
17 micron	4.45	1.02	3.36	0.07
53 micron	6.30	3.32	2.94	0.04

% Carbon by mass determined by the Analytical Laboratory at UCSB using a Control Equipment Corporation Model 240XA Elemental Analyzer.

TABLE 2a

Properties of Flocs as a Function of Sediment Concentration.

Natural Sediments from the Detroit River.

Concentration (mg/L)	Median Steady-State ¹ Floc Diameter (μm)	Time to Floc Size Equilibrium (hrs)	Settling ² Speed ($\mu\text{m/s}$)	Floc ³ Density (g/cm^3)
2	4500*	228	9700	1.0009
10	1330	63	7900	1.008
100	244	8.5	1685	1.05
500	48	4.5	511	1.41
2,000	24	2.5	216	1.69
10,000	17	1.2	189	2.20

1. Floc diameter measured by a Malvern 3600E Particle Sizer.
2. Settling speed directly measured in a settling tube.
3. Floc density determined by Stokes Law

*One floc

TABLE 2b

Properties of Flocs for Natural Sediments from the Detroit River.

Sediment Concentration of 500 mg/L.

Original Sediments were 53 μm Size Fraction.

Sediments	Median Steady-State Floc Diameter (μm)	Time to Equilibrium (hrs)	Settling Speed ($\mu\text{m/s}$)	Floc Density (g/cm^3)
Untreated	80	4.2	1751	1.50
Crushed to 14 μm	45	3.5	891	1.81
Organics stripped	73	5.0	1787	1.62
Organics stripped and Crushed to 14 μm	30	4.5	491	2.00

TABLE 3

Partition Coefficients for Different Size Fractions of Sediments.

Size	$\log K_p$	$\log K_{oc}$	$\log K_p$ (stripped)
3 micron	4.0	5.88	2.8
7 micron	3.7	5.57	2.7
17 micron	3.6	5.54	2.3
53 micron	3.8	5.39	2.6

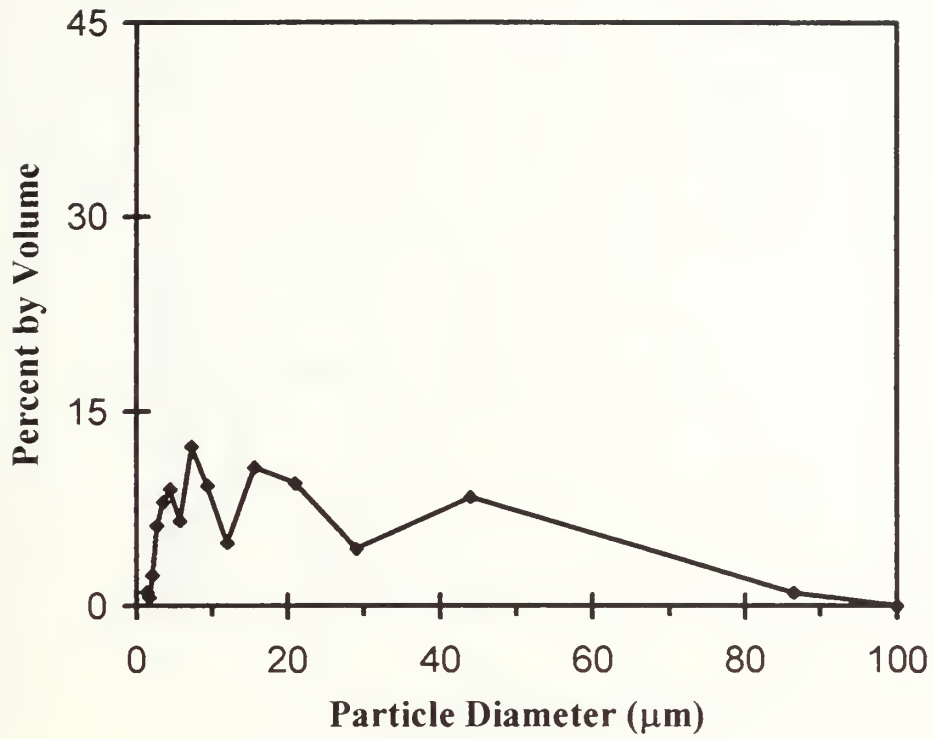


Figure 1a: Particle size distribution. Natural sediments from the Detroit River

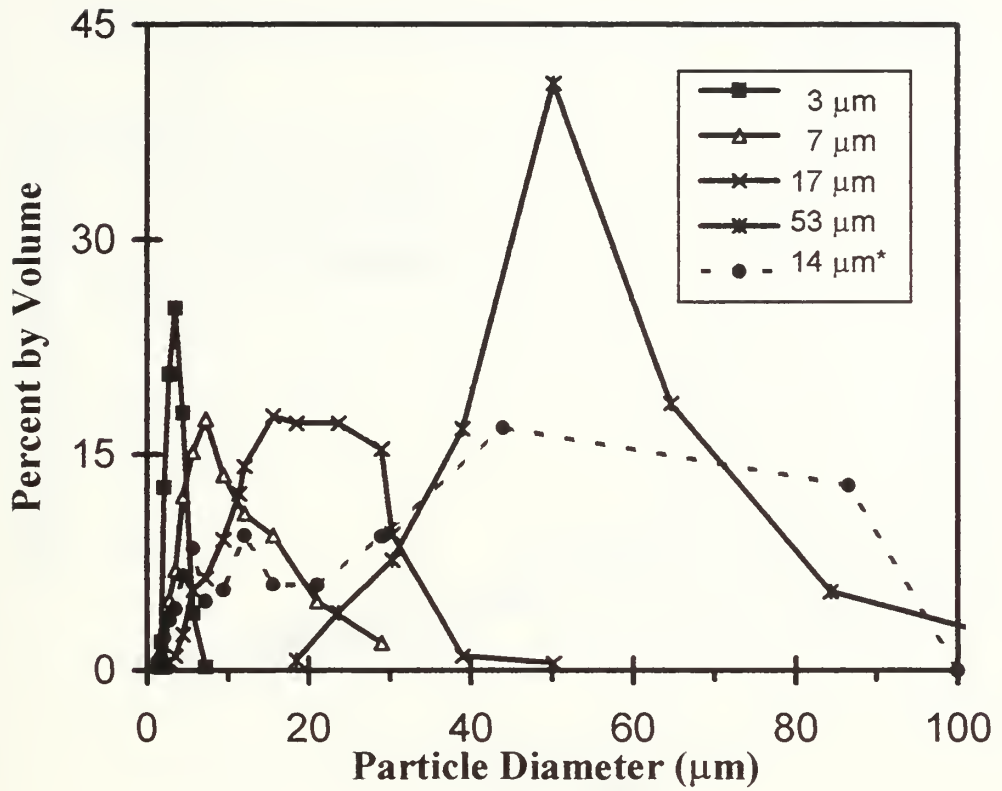


Figure 1b: Particle size distributions. Size-fractionated sediments of Detroit River sediment

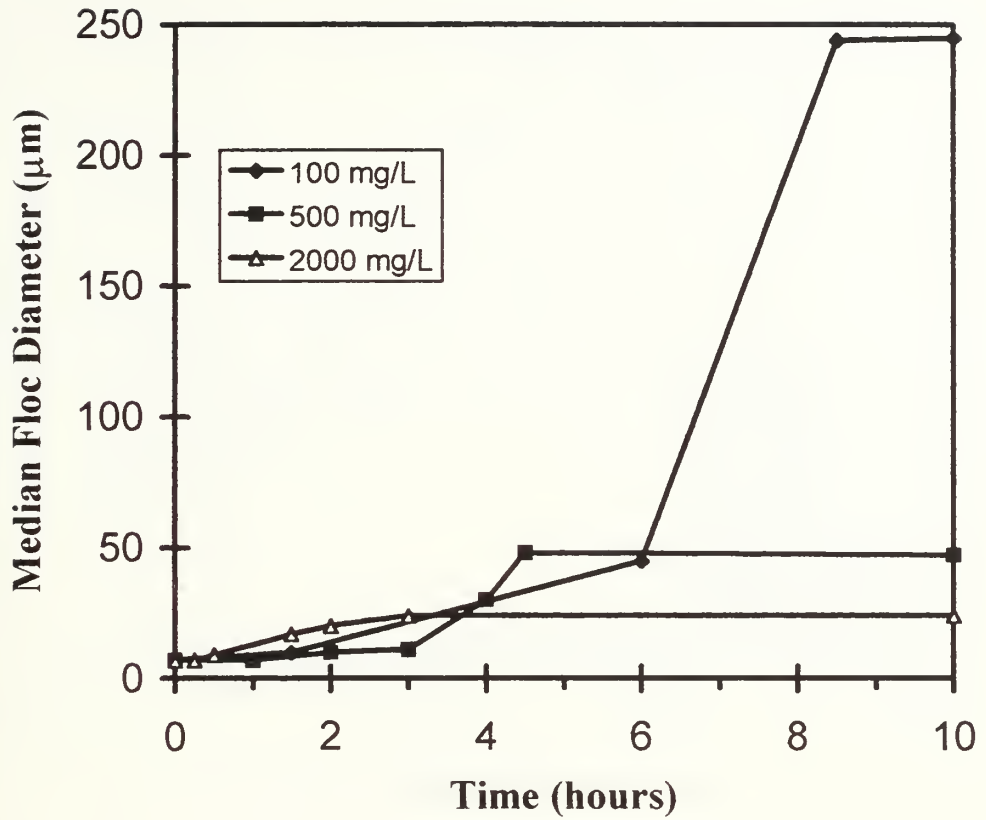


Figure 2: Floc median diameter as a function of time for natural sediments of the Detroit River at 100, 500, and 2000 mg/L.

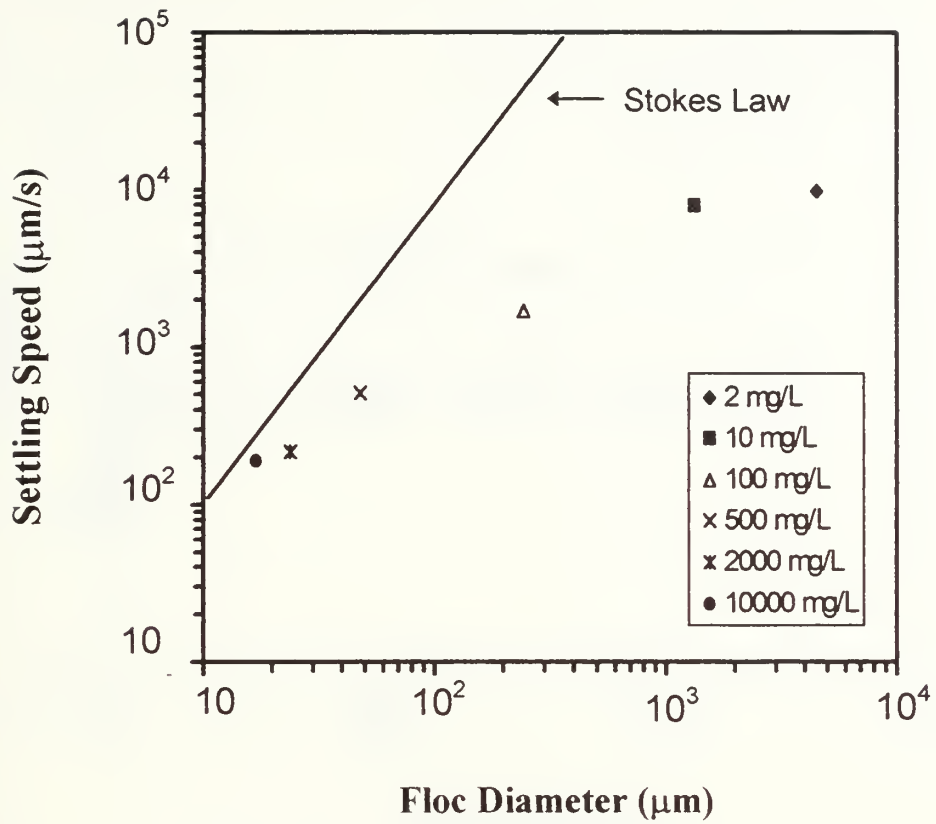


Figure 3: Floc settling speed as a function of floc diameter for natural sediments of the Detroit River. Steady state conditions.

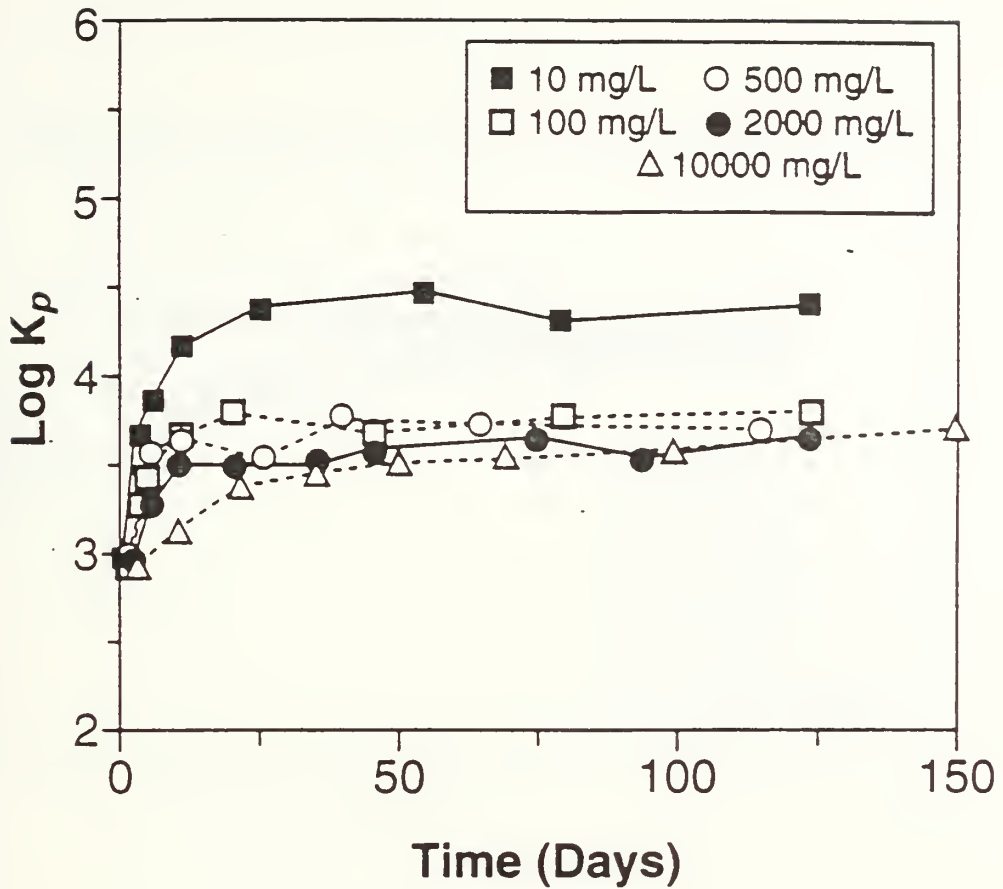


Figure 4: Batch experiments for adsorption of HCB dissolved in tap water to Detroit River sediment. HCB is dissolved in tap water filtered to 0.2 μm . After mixing for five days the HCB/tap water mixture is filtered by a 1 μm filter. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment concentrations of 10, 100, 500, 2000, and 10,000 mg/L. Previous experiments [7].

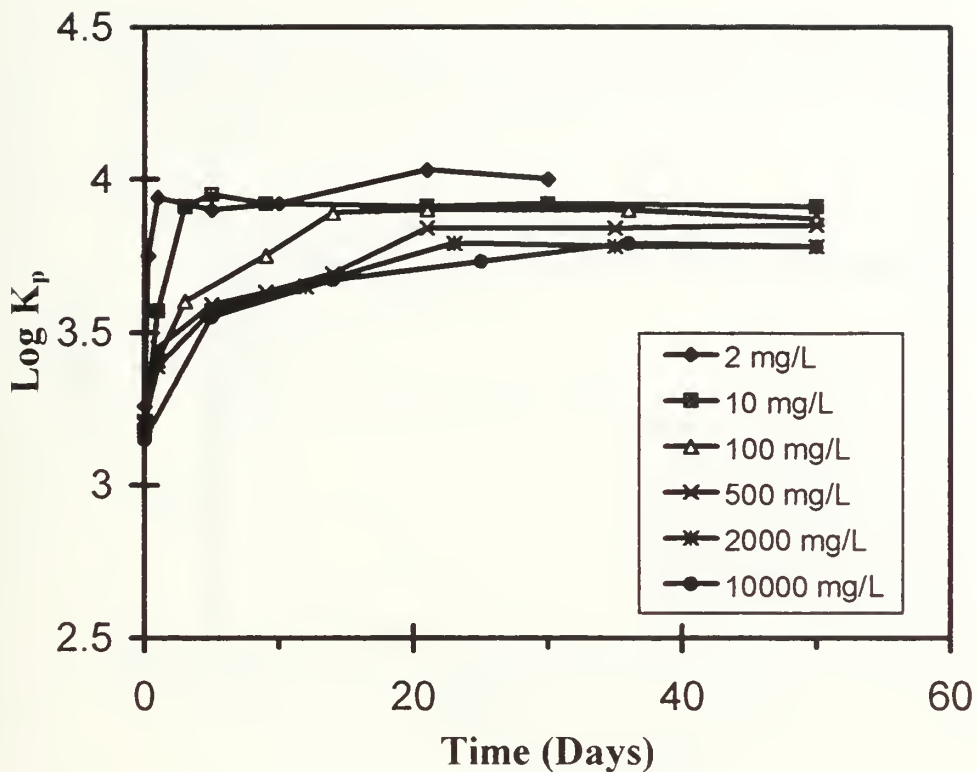


Figure 5: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment concentrations of 2, 10, 100, 500, 2000, and 10,000 mg/L. Experiments are prepared with pure water.

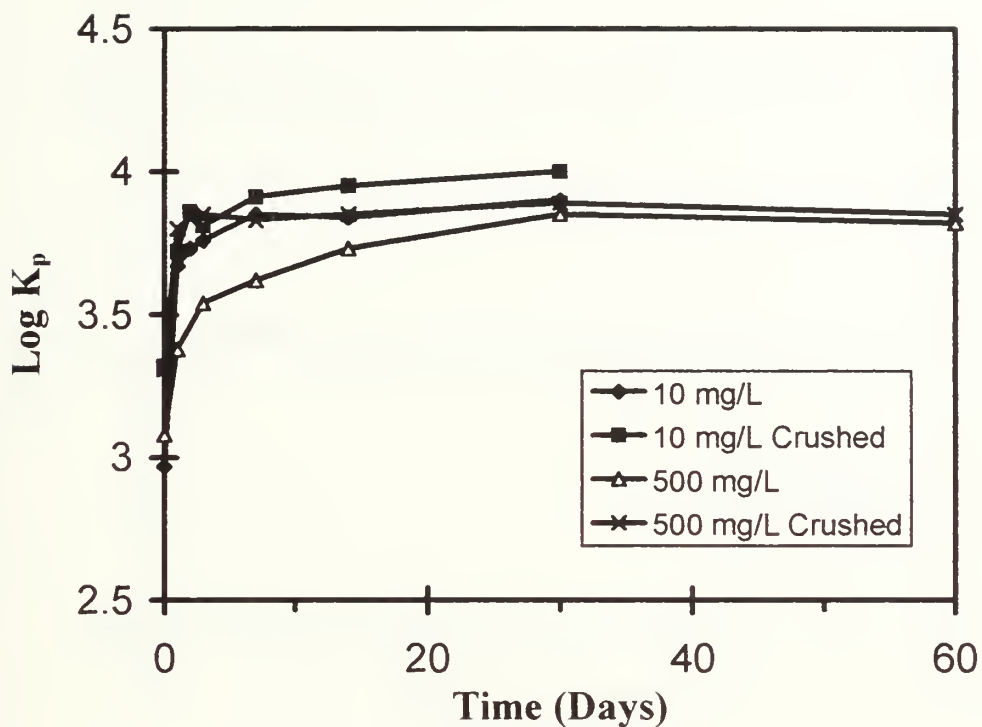


Figure 6: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. $\text{Log } K_p$ (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for $53 \mu\text{m}$ sediment at 500 and 10 mg/L, standard and crushed to $14 \mu\text{m}$.

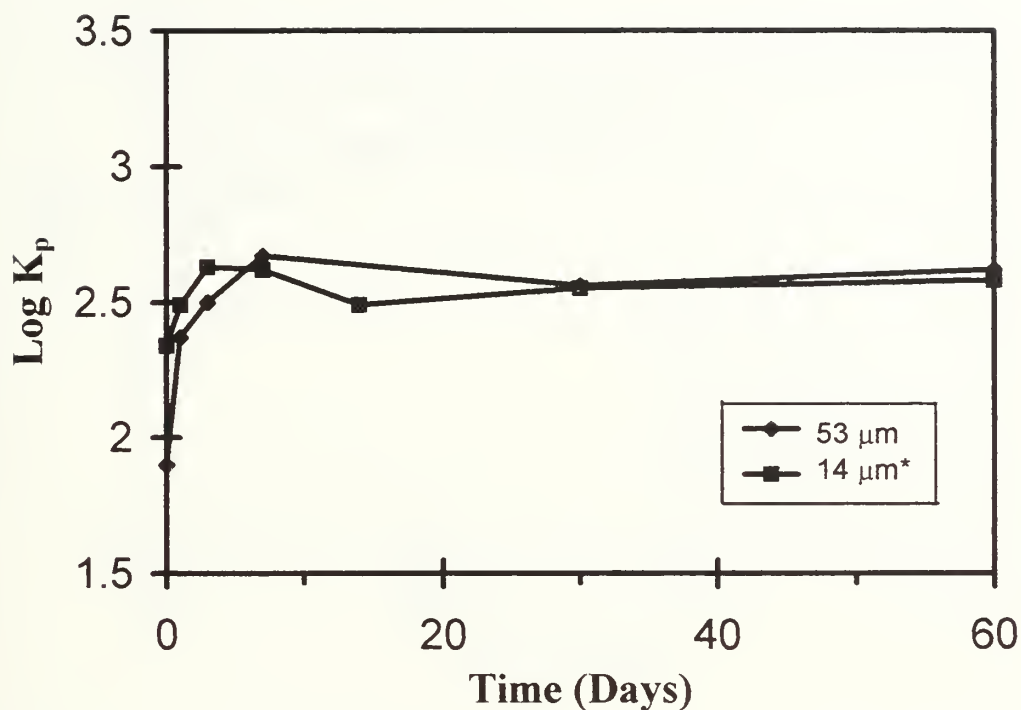


Figure 7: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 53 μm sediment at 500 mg/L. Sediment was first stripped of organic material using NaOCl. 14 μm^* is crushed 53 μm sediment.

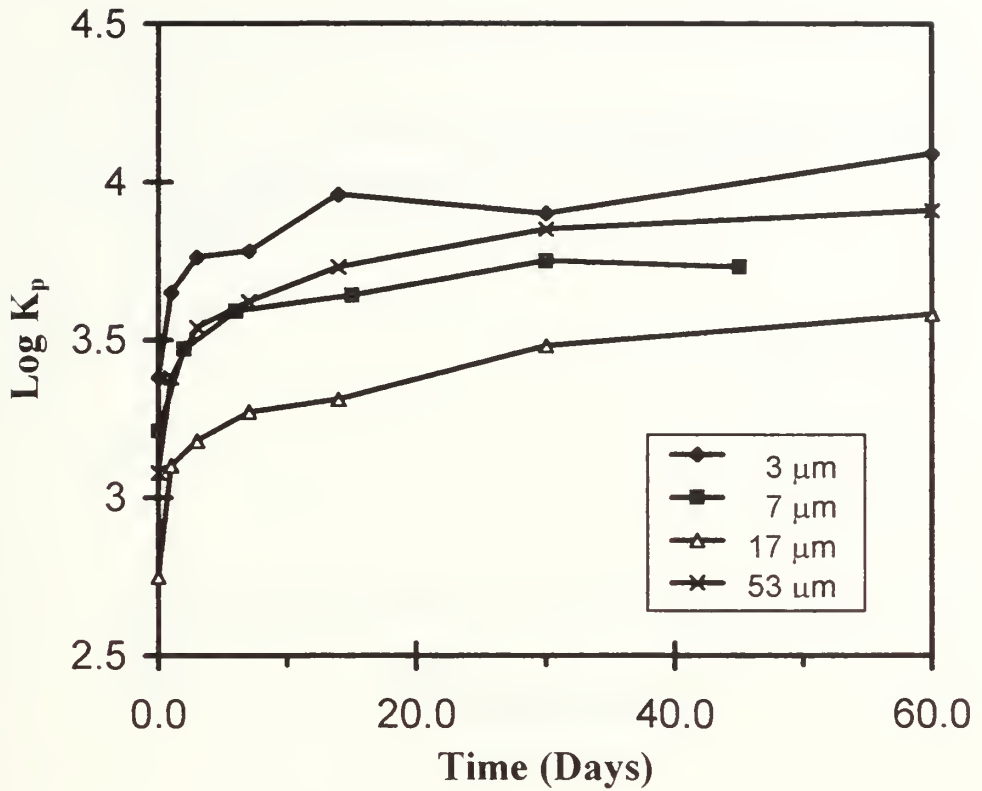


Figure 8: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. $\text{Log } K_p$ (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 500 mg/L sediment at 3, 7, 17, and 53 μm size fractions.

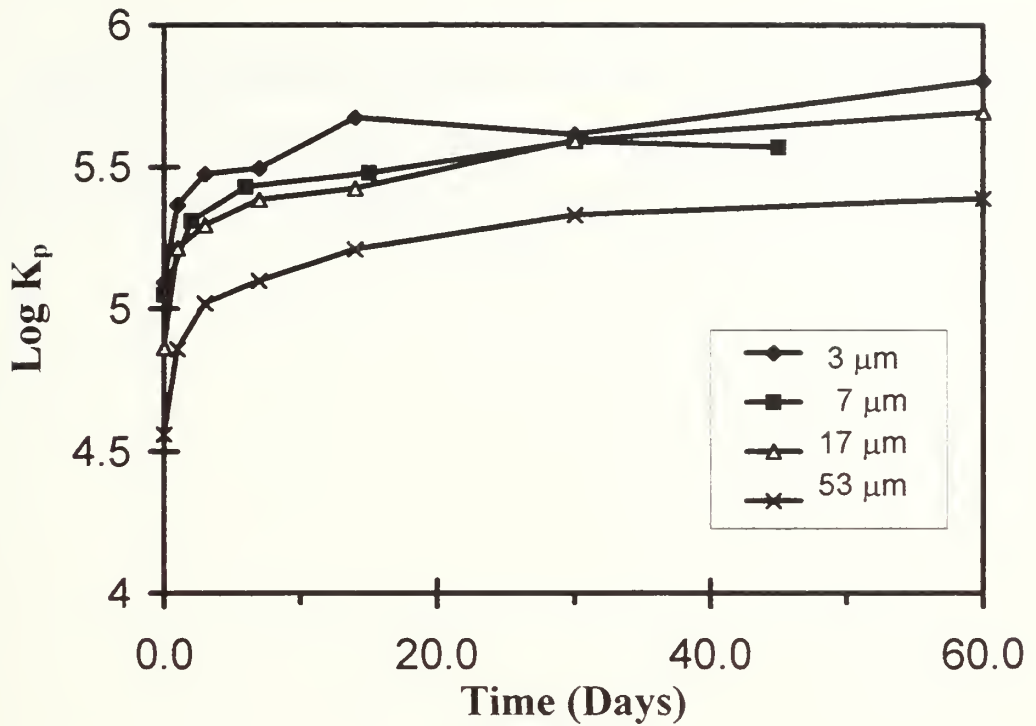


Figure 9: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 500 mg/L sediment at 3, 7, 17, and 53 mm size fractions. K_p has been normalized to organic carbon, K_p/f_{oc} .

APPENDIX A

Additional experiments are presented that were conducted with natural sediments from the Detroit River. Procedures used are the same as described previously. All experiments are of batch type, one sample jar for one data point.

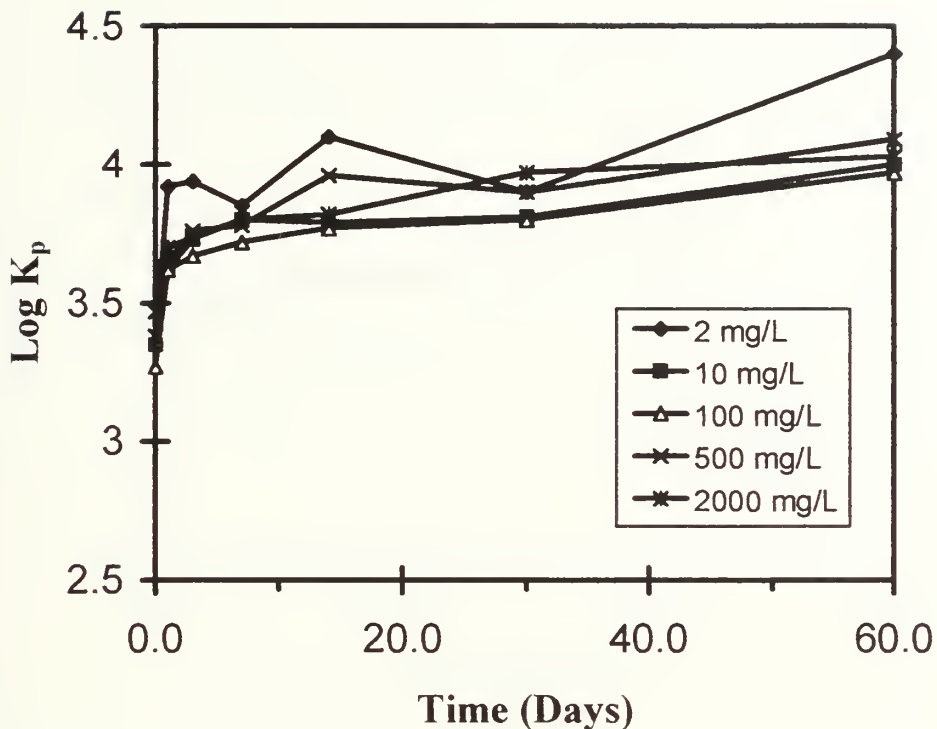


Figure A1: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 3 μ m size fraction of sediments.

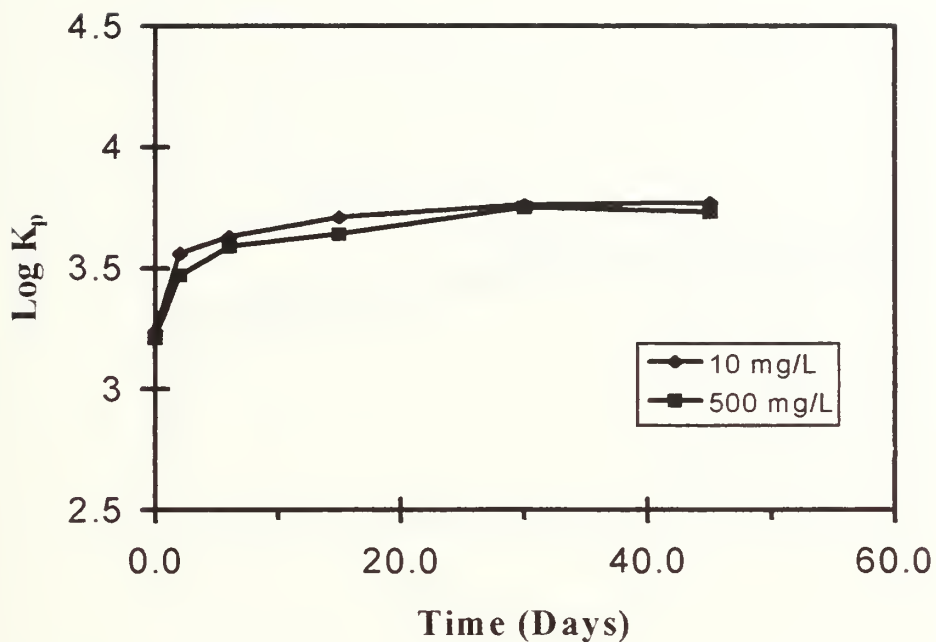


Figure A2: Batch experiments for adsorption of aqueous HCB to Detroit River sediment. Log K_p (K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 7 μm size fraction of sediments.

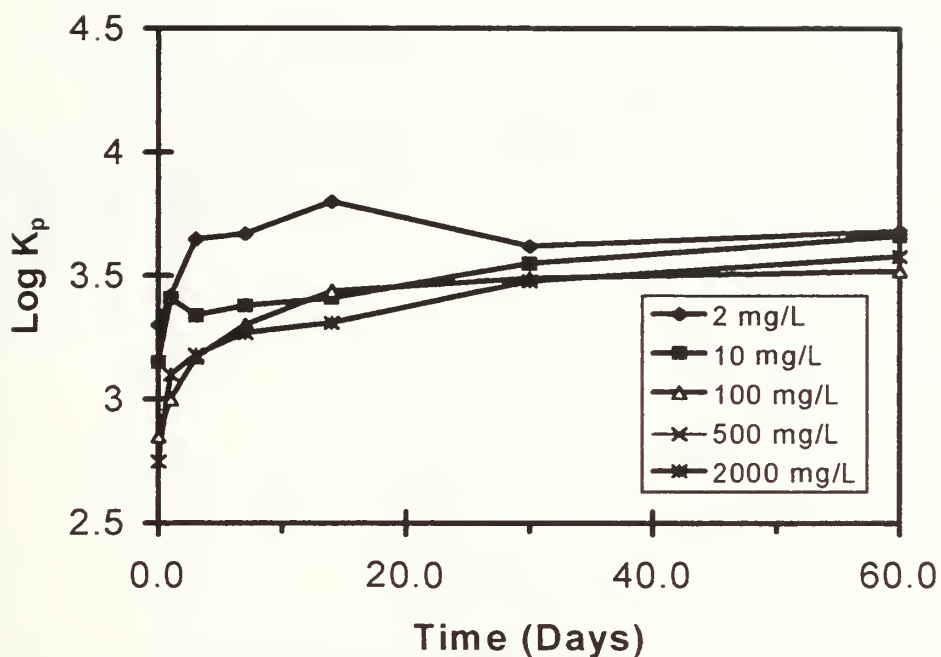


Figure A3: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for 17 μm size fraction of sediments.

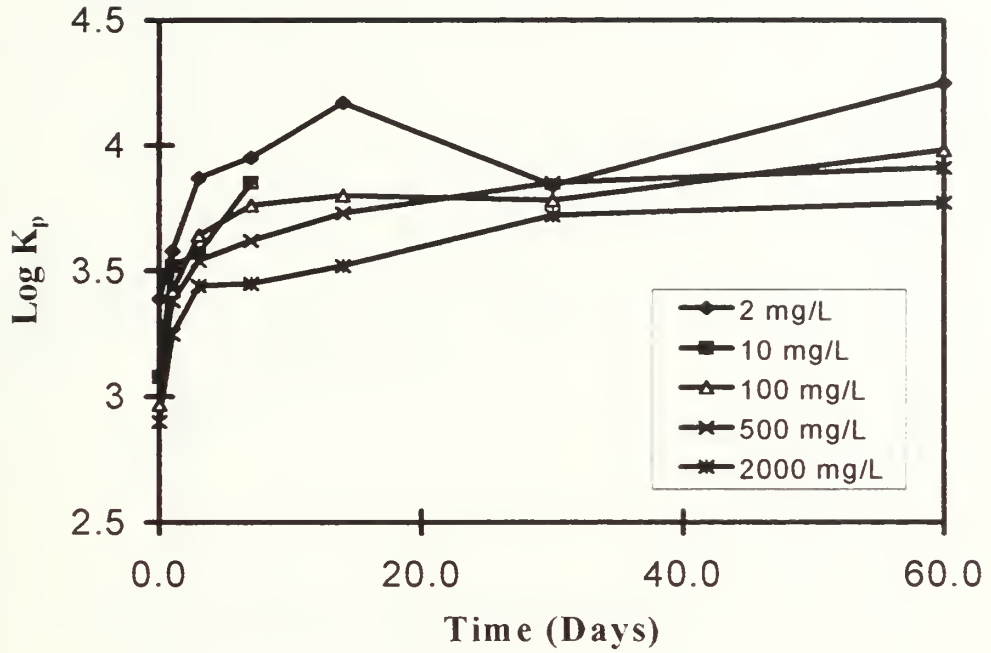


Figure A4: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. $\text{Log } K_p$ ($\text{Log } K_p = \text{ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution}$) as a function of time for 53 μm size fraction of sediments.

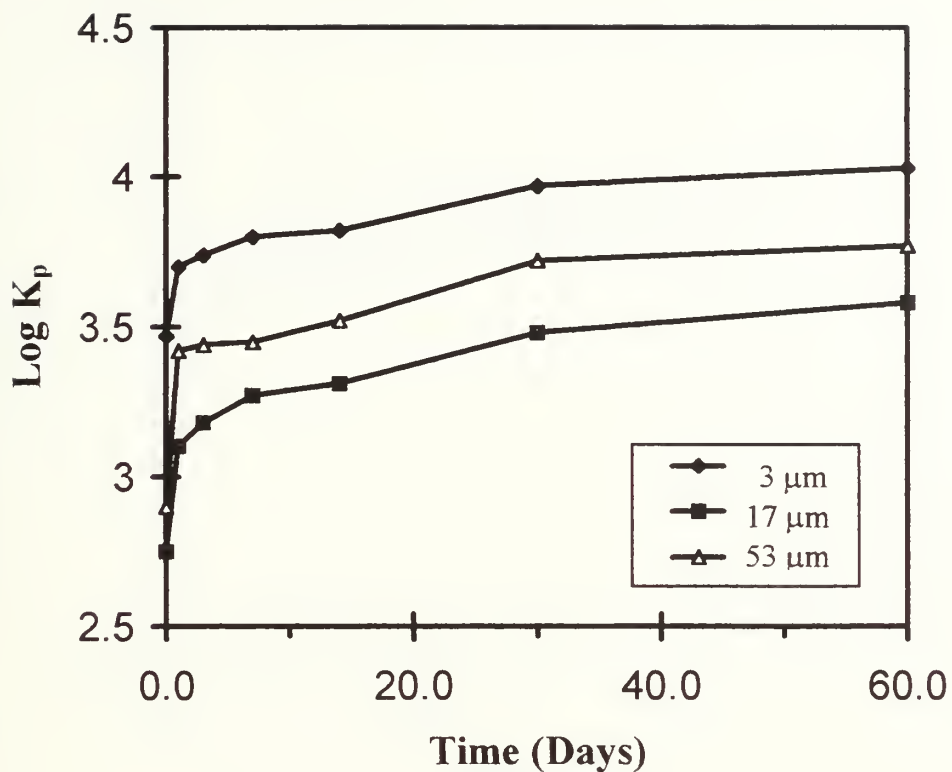


Figure A5: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time at 2000 mg/L.

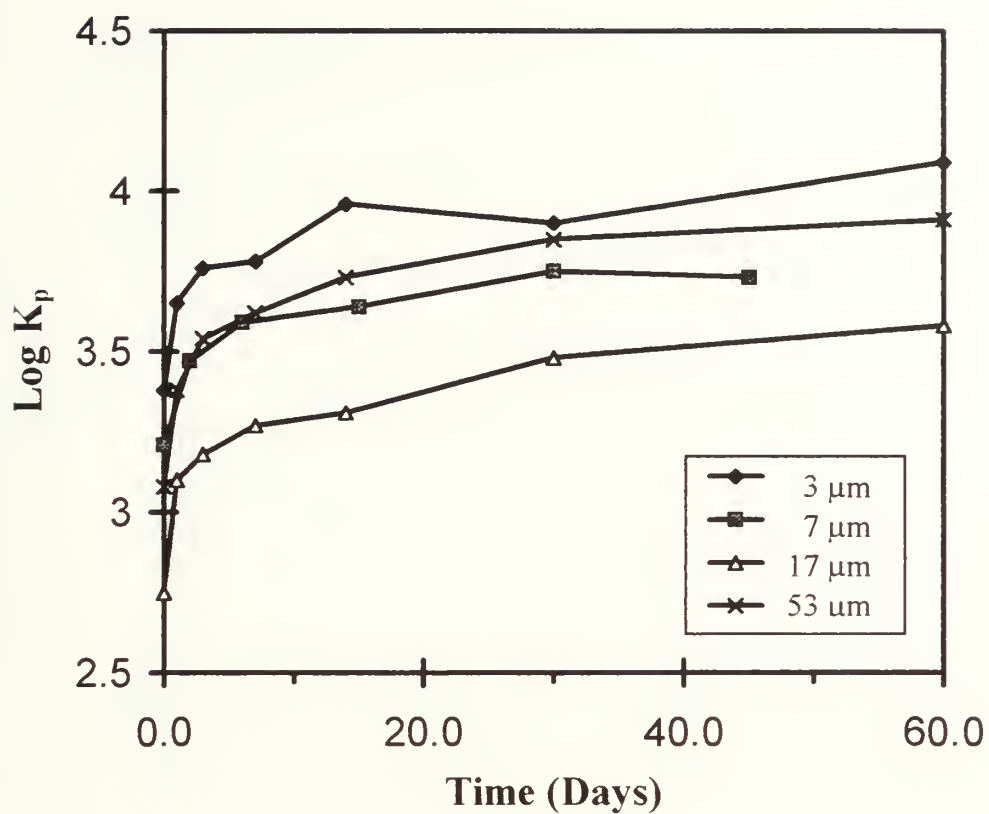


Figure A6: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. $\text{Log } K_p$ ($\text{Log } K_p = \text{ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution}$) as a function of time at 500 mg/L.

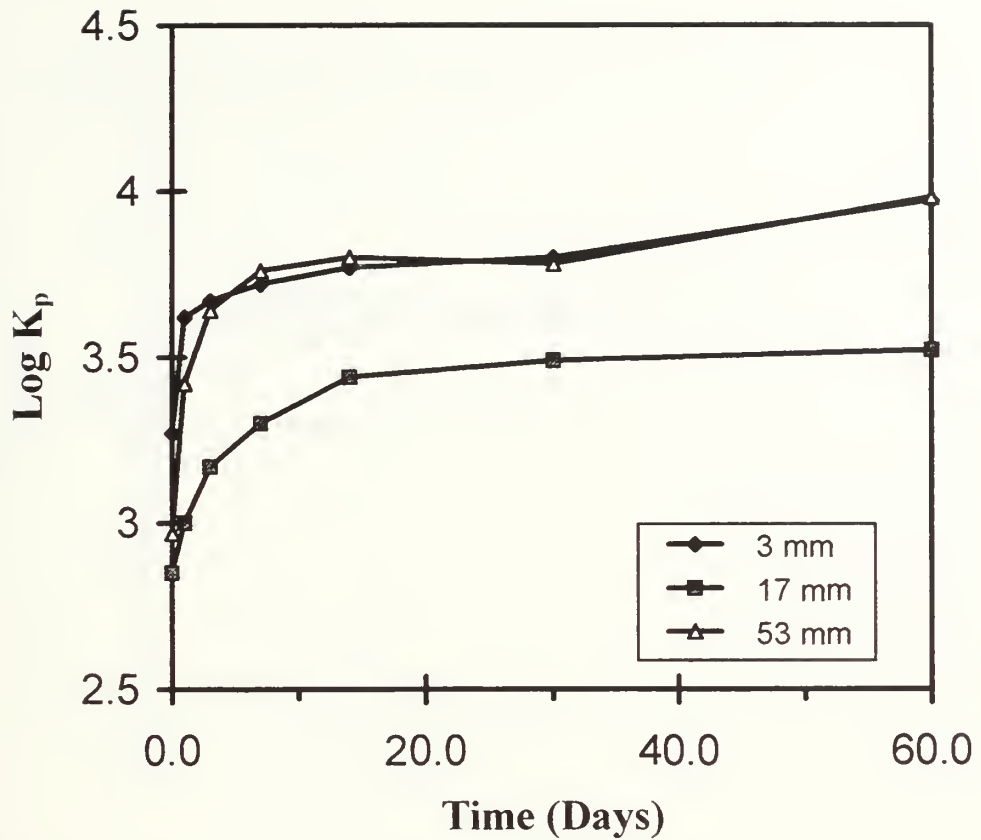


Figure A7: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. $\text{Log } K_p$ ($\text{Log } K_p = \text{ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution}$) as a function of time for sediment at 100 mg/L.

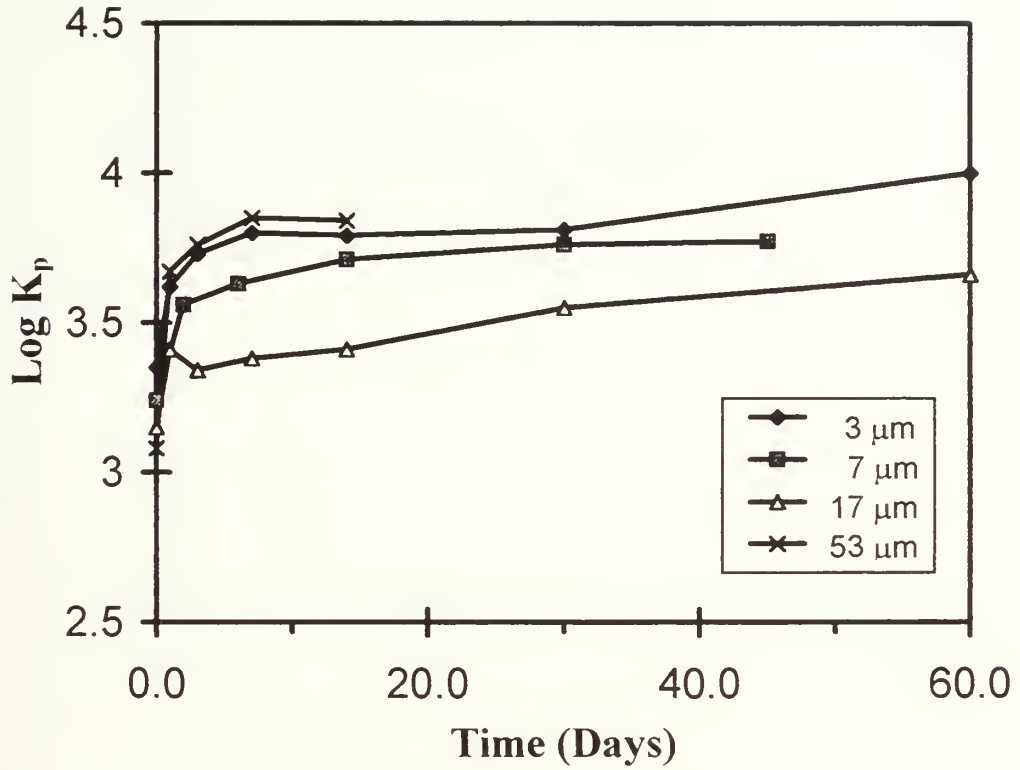


Figure A8: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 10 mg/L.

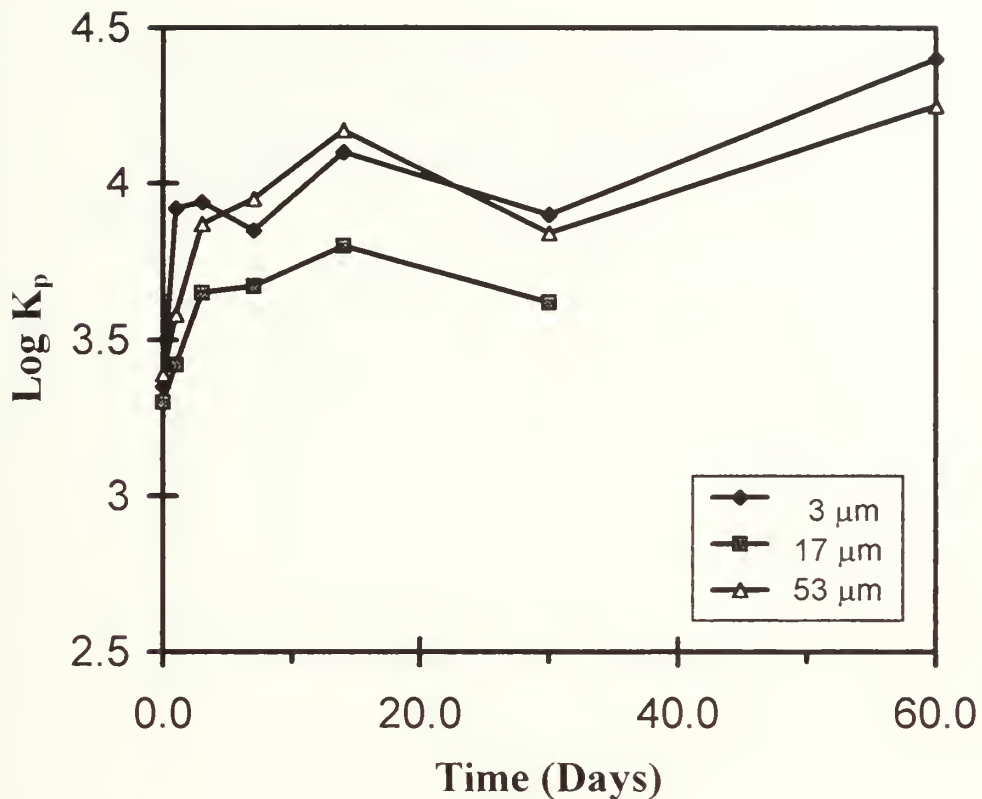


Figure A9: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 2 mg/L.

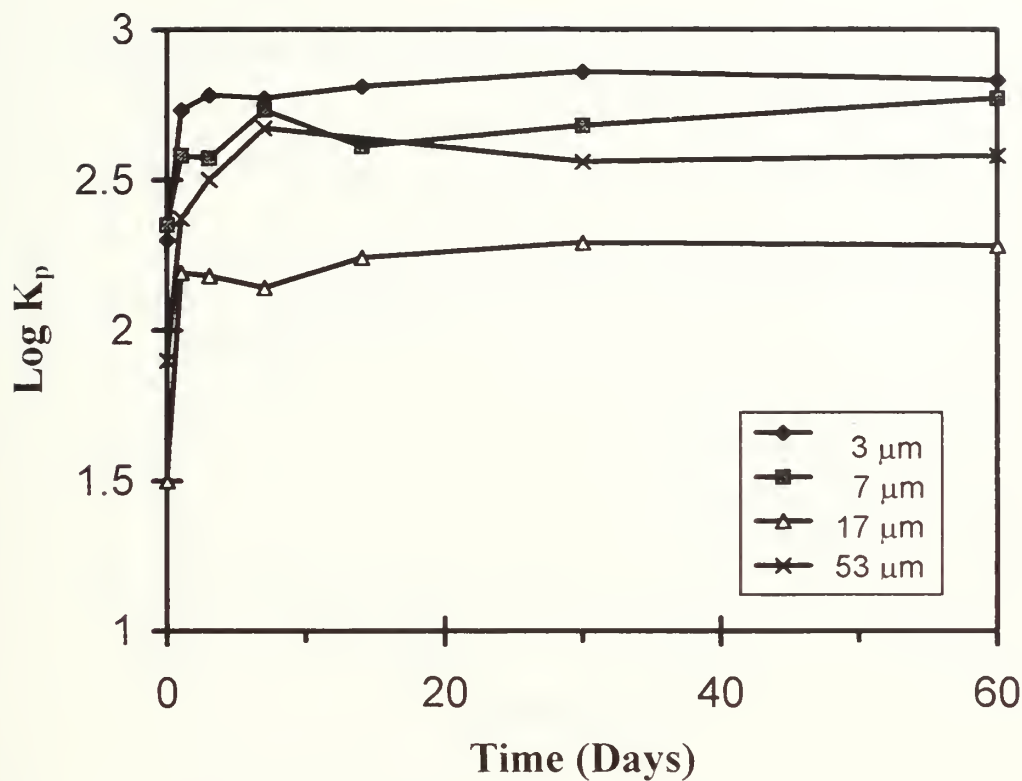


Figure A10: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediments at 500 mg/L stripped of organic material using NaOCl.

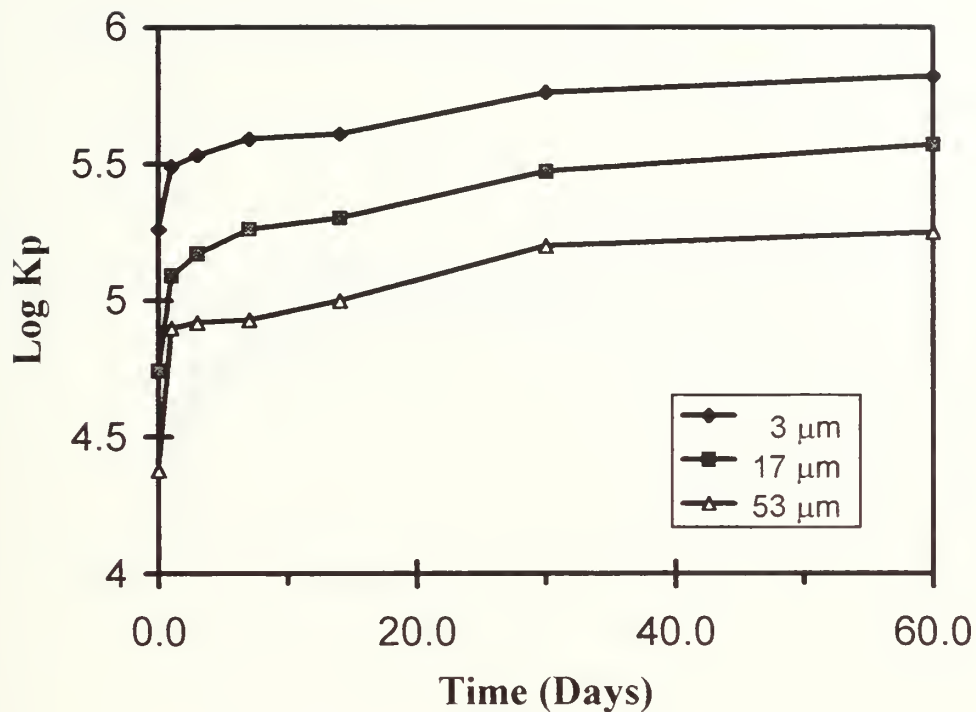


Figure A11: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 2000 mg/L normalized to organic carbon, K_p/f_{oc} .

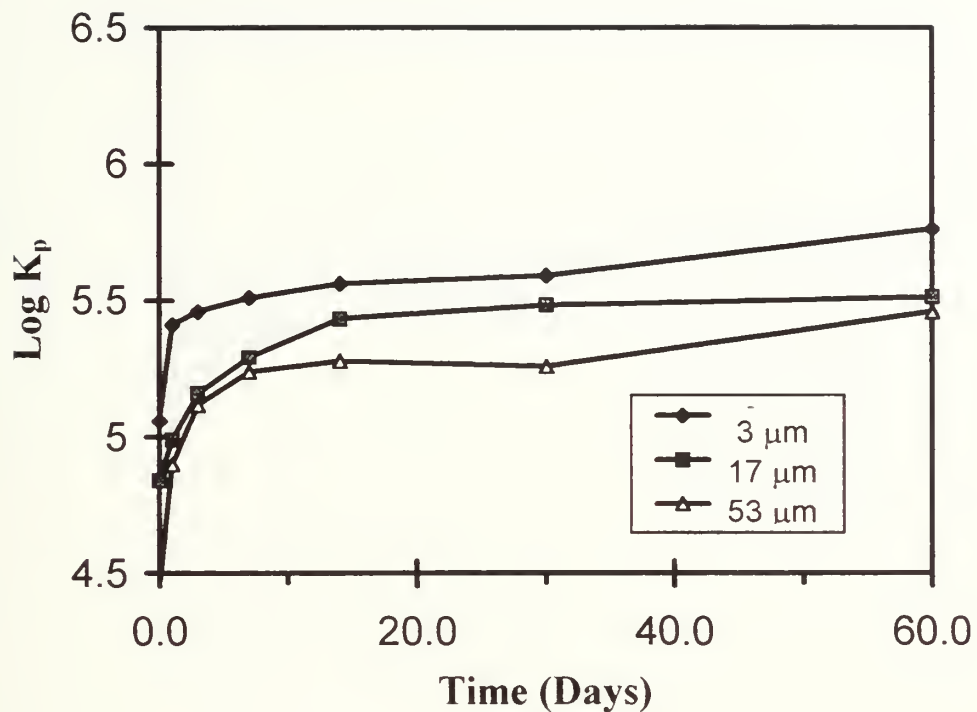


Figure A12: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 100 mg/L normalized to organic carbon, K_p/f_{oc} .

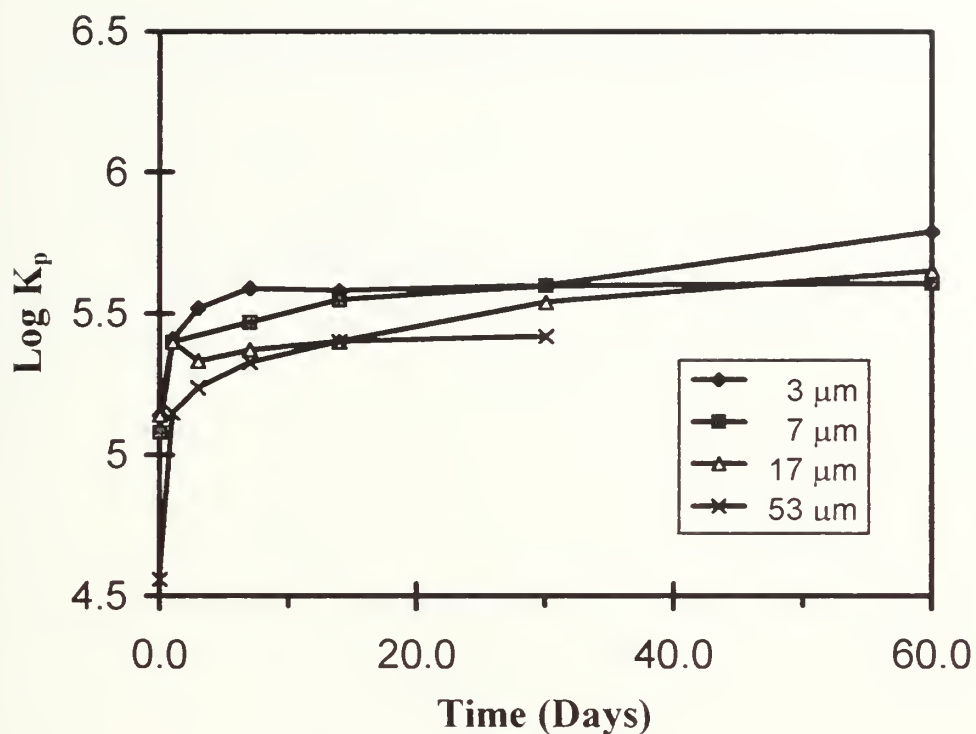


Figure A13: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 10 mg/L normalized to organic carbon, K_p/f_{oc} .

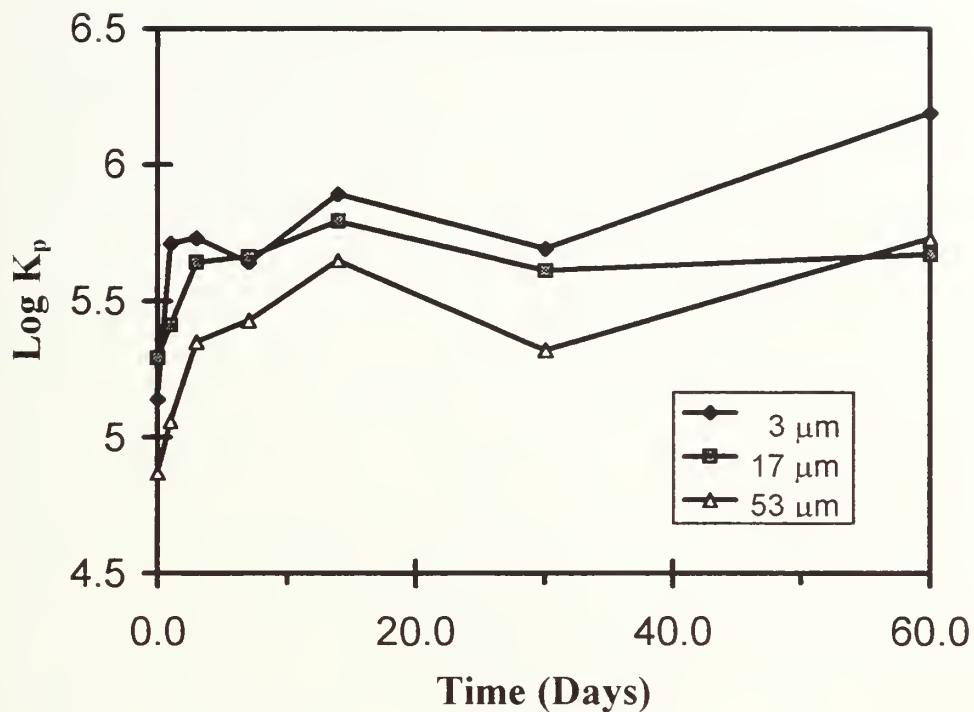


Figure A14: Batch experiments for adsorption of aqueous of HCB to Detroit River sediment. Log K_p (Log K_p = ratio of concentration of HCB adsorbed on sediment to the concentration of HCB dissolved in solution) as a function of time for sediment at 2 mg/L normalized to organic carbon, K_p/f_{oc} .

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